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(54) **REDUCTION DE LA FORMATION BENZENE DANS LES FORMULATIONS DE PEROXYDE DE BENZOYLE**

(54) **REDUCTION OF BENZENE FORMATION IN DIBENZOYL PEROXIDE FORMULATIONS**

(57) La présente invention concerne, de manière générale, une méthode pour réduire la vitesse de formation de benzène libre dans les formulations de BPO et la quantité formée. La méthode comprend l'addition d'au moins un accepteur de radicaux libres dans lesdites formulations en une quantité efficace pour réduire la vitesse de décomposition du BPO. L'invention concerne également des formulations de BPO caractérisées par une vitesse de décomposition réduite et une stabilité améliorée et qui contiennent une quantité efficace d'au moins un accepteur de radicaux libres.

(57) The present invention generally relates to a method for reducing the rate and amount of free benzene formation in BPO formulations. The method comprises adding at least one free-radical scavenger to said formulations in an amount effective to reduce the rate of BPO decomposition. The invention also relates to BPO formulations having reduced decomposition rates and improved stability which contain an effective amount of at least one free-radical scavenger added thereto.

ABSTRACT

The present invention generally relates to a method for reducing the rate and amount of free benzene formation in BPO formulations. The method comprises adding at least one free-radical scavenger to said formulations in an amount effective to reduce the rate of BPO decomposition. The invention also relates to BPO formulations having reduced decomposition rates and improved stability which contain an effective amount of at least one free-radical scavenger added thereto.

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REDUCTION OF BENZENE FORMATION IN DIBENZOYL PEROXIDE FORMULATIONS

Field of the Invention

The present invention generally relates to a method for the reduction of free benzene formation in diacyl peroxide formulations.

Background of the Invention

Dibenzoyl peroxide ('BPO') is commonly used as a free-radical initiator for the synthesis of various types of polymers, graft copolymers and interpenetrating networks that are applied in the manufacture of industrial and consumer products, and as curing agents and cross-linking agents in polymer industries. Recently, however, it has been discovered that BPO formulations such as pastes, emulsions and suspensions based on organic plasticizers, whether in the presence or absence of water, show continuously increasing levels of free benzene throughout their useful lifetime. This free benzene is formed due to the slow decomposition of the BPO over time.

Bull. Envir. Contam. Toxicol. (1994) 53: 747-752 provides a detailed discussion of the formation of benzene by hardeners containing BPO and phthalates, and concludes that BPO and phthalate containing hardeners may be a potential source of exposure to consumers as well as for industry workers.

Because of the known carcinogenic properties of benzene, minimization of its formation is highly desirable. Accordingly, it is an object of the invention to minimize the decomposition of BPO formulations over time, thus reducing the rate and amount of free benzene formation.

It is also an object of the present invention to provide BPO formulations having a substantially lower rate of free benzene formation. These and other objects are realized by the invention hereinafter described.

Summary of the Invention

The present invention generally relates to a method for reducing the rate of free benzene formation in BPO formulations. The method generally comprises adding at least one free-radical scavenger to said formulations in an amount effective to reduce the rate of BPO decomposition.

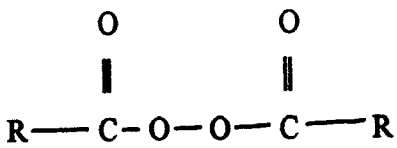
The invention also relates to BPO formulations having reduced decomposition rates which contain an effective amount of at least one free-radical scavenger added thereto.

Detailed Description of the Invention

The present invention broadly relates to a method for reducing the rate and amount of diacyl peroxide decomposition which comprises adding to said composition at least one free radical scavenger in an amount effective to reduce the rate of diacyl peroxide decomposition. The method of the present invention also minimizes the generation of hazardous by-products which are formed by the decomposition of diacyl peroxides. The invention also relates to a diacyl peroxide composition having improved stability and reduced decomposition rate which has added thereto, an effective amount of at least one free radical scavenger.

In another embodiment, the invention relates to a method for reducing the rate of free benzene and/or benzene derivative formation in BPO formulations based on organic plasticizers, such as pastes, emulsions, suspensions, dispersions and the like. More particularly, the present inventors have discovered that through the addition of select free-radical scavengers, the rate and amount of free benzene formation can be significantly reduced in BPO formulations without any direct loss in reactivity or adverse affects on the formulations themselves.

Dibenzoyl peroxides within the context of the present invention shall mean any diacyl peroxide which, upon decomposition, generates free benzene or benzene derivatives. Diacyl peroxides of this type generally correspond to those of the general formula:



wherein each R group may be the same or different and is selected from substituted or unsubstituted aryl, aralkyl, alkyl, alkaryl, and the like, with the proviso that at least one of said R groups contains a benzyl moiety. Preferred peroxides are dibenzoyl peroxide, 2,4-dichloro, ortho- and para-methyl derivatives of dibenzoyl peroxide. Dibenzoyl peroxide is the preferred peroxide to be employed in accordance with the present invention.

Any free-radical scavenger capable of reacting with the free-radical species in the BPO formulation can suitably be employed in the present invention. The normal decomposition pathway of BPO is the initial formation of benzoyloxy radicals followed by either decarboxylation with formation of the phenyl radical and hence benzene, and/or the attack of the benzoyloxy or phenyl radical on the BPO, sometimes referred to as induced decomposition, resulting in additional decomposition of the BPO. Without wishing to be bound to any particular theory of operation, it is believed that the free-radical scavenger reacts and/or traps the benzoyloxy radicals or phenyl radicals that are formed during the decomposition of the BPO, which prevents the formation of benzene by eliminating the precursors. The trapping of precursor radicals also slows induced decomposition of the BPO, which results in a formulation with superior stability over time.

Preferred free-radical scavengers include but are not limited to cinnamate esters, fumarate esters, maleate esters, natural fatty acids, oligomeric phosphonates, phenol derivatives,

thiobisphenolics, phosphites, polythiodipropionates, thioesters, propionate esters, quinones, vitamin compounds, triazinetrione derivatives, and the like. Specific examples of free-radical scavengers which are employable in the context of the present invention include but are not limited to:

1,2-bis(3,5-di-t-butyl-4-hydroxyhydrocinnamoyl)hydrazine (eg, Irganox® MD1024, Irganox is a registered trademark of Ciba-Geigy Inc.),

octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate (eg. Irganox® 1076),

tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane (eg. Irganox® 1010),

dibutyl fumarate,

dioctyl fumarate,

dibutyl maleate,

dibutyl and dioctyl maleate,

linoleic acid and oleic acid,

styrene phosphonic acid,

calcium bis[monoethyl(3,5-di-t-butyl-4-hydroxybenzyl) phosphonate] (eg. Irganox® 1425),

benzoic acid,

n-nonyl phenol ("NNP"),

2,6-di-t-butyl-4-methylphenol ("BHT"),

trisnonylphenylphosphite ("TNPP"),

t-butyl catechol ("TBC"),

triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-ethylphenyl) propionate] (eg., Irganox® 245),

pyrrolidones,

vitamin A (all-trans-retinol),

vitamin C (ascorbic acid),

vitamin E (2,5,7,8-tetramethyl-2-(4',8',12'-trimethyltridecyl)-6-chromanol, DL-*a*-tocopherol],

1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (eg., Irganox® 3114),

hydroquinone ("HQ"),

toluhydroquinone ("THQ"),
p-benzoquinone ("pBQ"),
mono-t-butylhydroquinone ("MTBHQ")
2,5-di-t-butylhydroquinone ("DTBHQ"),
hydroquinone monomethyl ether ("HQMME"), and the like.

The most preferred free-radical scavengers are BHT, Vitamin E, Irganox®1010, Irganox®1425 and NNP. BHT is especially preferred.

In order to realize the objectives of the present invention, at least one free-radical scavenger is added to the BPO formulation in an amount effective to increase the stability of said formulation. Obviously, the amount of free-radical scavenger required is a function of the type of scavenger to be employed and the amount of BPO in the formulation. Most BPO formulations generally contain from about 3% to about 85% by weight BPO, more typically, from about 25% to about 60% BPO. Regardless of the BPO concentration, it is well within the abilities of one of ordinary skill in the art to determine, without undue experimentation, the amount of free-radical scavenger required to decrease the decomposition rate of the BPO, thereby increasing the stability of said formulation and reducing the rate and amount of free benzene formation.

An effective amount of free-radical scavenger is, in most cases, in the range of between about 0.001% by weight to about 10% by weight based on the diacyl peroxide formulation. More preferably, an effective amount of the free-radical scavengers is in the range of 0.01 - 5%. In a most preferred embodiment the free-radical scavenger comprises from about 0.1-3% by weight of formulation.

In a preferred embodiment, the invention contemplates a BPO formulation having a substantially reduced rate of free benzene formation wherein said formulation comprises BPO, and at least one free-radical scavenger in an amount effective to reduce the rate of BPO

decomposition in said formulation. The BPO formulation can be in the form of a paste, emulsion, suspension, gel and the like. The types and amounts of free-radical scavengers are the same as hereinbefore described.

In another embodiment, the invention contemplates a BPO formulation having a substantially reduced rate of free benzene formation wherein said formulation comprises 3-60 wt% BPO, and 0.001-10 wt%, preferably 0.1 to 5wt% of at least one free-radical scavenger in an amount effective to reduce the rate of BPO decomposition in said formulation.

In a third preferred embodiment, the invention contemplates BPO formulation with reduced benzene formation which comprises:

3-60 wt%	BPO
10-30 wt%	water
0.5-95 wt%	plasticizers
0-10 wt%	surfactant
0-10 wt%	rheologicial additive
0-5 wt%	pigments
0.01-5 wt%	scavenger

An optimum formulation preferably comprises:

25-60 wt%	BPO
5-50 wt%	water
5.5-50 wt%	plasticizers
0-10 wt%	surfactant
0-10 wt%	rheological additive
0-5 wt%	pigments
0.1-3wt%	scavenger

The invention will now be illustrated by the following nonlimiting examples.

Example 1 - Paste Preparation

A kneader was charged with BPO (BPO 75% in water) isodecyl benzoate, water, and zinc stearate. After 10 minutes of mixing, polymeric thickener, Carbopol® 690 (Carbopol® is a registered trademark of B.F. Goodrich Inc.) was added and mixed for an additional 20 minutes. Finally, nonionic surfactant, Tergitol® XD, was added and the mixture was blended for 30 minutes. (Tergitol® is a registered trademark of the Union Carbide Corporation). A smooth, uniform paste was produced.

Test Method Descriptions:

Akzo Nobel Test Method 220ASSAY.1

Assay determination was conducted on 0.5 g samples for BPO paste and 1.0 g for resin anchor catalyst formulations. All samples were run in duplicate.

The sample was added to a 250ml flask, followed by the addition of 25 ml of acetone. 0.5 ml of 10% hydrochloric acid and 3 ml of potassium iodide were then added, and the flask was swirled to mix the ingredients. The inside wall of the flask was washed down with acetone. After standing one minute, the mixture was titrated with 0.1N sodium thiosulfate. Assay was determined by the following calculation:

$$\% \text{ peroxide assay} = (A \times N \times F) \div \text{sample weight in grams}$$

wherein, A = Volume of the thiosulfate used,

N = Normality of the thiosulfate

F = 12.11 for BPO

Akzo Nobel Internal Method Of Analysis AR/88.1 HPLC

Benzene determination was conducted on prepared pre-weighed 0.5 g samples sealed in 20 ml headspace vials. All samples were run in duplicate.

5 ml of hexane was added by syringe through the septa. The sample was agitated and allowed to stand for 10-15 minutes. Another 5 ml of hexane was then added. An empty syringe was used to allow the air to escape from the vial. The sample was ultrasonicated for approximately 5 minutes to extract the benzene, with aliquots of approximately 3 ml withdrawn for analysis.

In the reverse phase liquid chromotography analysis, the following conditions/procedures were used:

- 20 ul injection with WISP A/S
- 15 cm x 4 mm ODS column
- UV at 205 nm
- Time 0 minutes: 1 ml/min 70/30 acetonitrile/water with 0.05m acetic acid
- 4 minute gradient over 2 minutes to 100% acetontrile at 2 ml/min, held for 5 minutes, then reversed to original conditions over 2 minutes and held for a total run time of 20 minutes.
- The minimal detection limit for the instrument was 0.5 ppm benzene. Due to dilution and interfering peaks present in the sample chromatograms, the minimal quantifiable amount was 20 ppm.

Employing the following test methods, a 55% BPO paste was prepared in accordance with the present invention and tested for performance of benzene reducing additives. Performance was measured against a neat paste prepared in the same manner, except that no free radical scavenger was added.

Samples were stored for two weeks at 50°C to accelerate BPO decomposition. This is intended to simulate typical free benzene formation at ambient temperatures over the useful life of the paste product. Both free benzene and assay loss were monitored. A neat paste sample maintained at 20°C served as the control for all subsequent comparisons. The benzene level of

this control remained fairly constant during testing in the range of 400ppm. The data is summarized in Table 1, below:

Table 1 - Performance of Benzene Reducing Additives in 55% BPO Paste

	Benzene content (ppm)	Assay (%BPO)	
	Increase	**% change**	**% change**
Neat paste	2653	663%	-3.1%
Dibutyl fumarate	1442	361%	-12.6%
Dioctyl fumarate	1317	329%	-1.1%
Styrene phosphonic acid	1351	338%	0.5%
Linoleic acid	2312	578%	-6.8%
Benzoic acid	1013	253%	-5.1%
Irganox 245	1734	434%	-3.5%
Irganox 1010	332	83%	0.0%
Irganox MD 1024	375	94%	-0.9%
Irganox 1076	1924	481%	2.2%
Irganox 1425	251	63%	0.0%
Irganox 3114	650	163%	-2.6%
BHT	267	67%	-1.8%
NNP	454	113%	-3.4%
Vitamin E	817	204%	-5.4%
Dibutyl maleate	1835	459%	-0.5%
Dioctyl maleate	1223	306%	-2.5%
Oleic acid	3094	774%	-4.5%

Benzene % change was calculated by the following formula:

[(ending benzene content - starting benzene content) ÷ starting benzene content] x 100

Assay % change for the BPO was calculated in accordance with the following formula:

[(ending BPO content - starting BPO content) ÷ starting BPO content] x 100

The data indicate that the rate of free benzene formation in the formulations containing the free-radical scavengers in accordance with the present invention is, in most situations, dramatically lower than in the formulations containing no scavenger. Furthermore, the stability of the formulations of the present invention, as demonstrated by the % assay loss of BPO was markedly improved over compositions which lacked free-radical scavengers in accordance with the present invention.

For example, over the two week period at 50°C, the neat paste increased in benzene content by 2653 ppm. This is equivalent to a 663% increase over the room temperature control paste, and is indicative of the degree of benzene formation expected over the paste's useful lifetime. The assay of the neat paste decreased by 1.8% over the same two week period.

The paste sample containing the free radical scavenger BHT increased in benzene content by only 267 ppm, which is equivalent to a 67% increase over the room temperature control paste. In addition, the assay of the BHT-containing paste decreased by only 3.1%. Similar results were observed for other pastes containing free radical scavenger in accordance with the present invention.

Resin Anchor System

To demonstrate the effect of the addition of free-radical scavenger on cure behavior, a resin anchor system was tested with the additives listed in Table 2. The formulation consisted of

an unsaturated polyester resin/calcium carbonate "A" component and a BPO/calcium carbonate "B" component to which 0.1% of additive was added.

A Haake Rheocord 90 rheometer with delta blades at 60 rpm was used for cure determination. The "A" component was added to the mixing bowl at ambient temperature conditions. After 30 seconds, the "B" component was injected into the bowl with a syringe, and cure response was obtained by measuring torque as a function of time. The data is tabulated in Tables 2 and 3, below.

Table 2 - Performance of Benzene Reducing Additives in Resin Anchor "B" Component

Additive	Assay loss, % BPO change after x weeks @ 50°C		Benzene level, ppm after x weeks @ 50°C		
	1	2	0	1	2
None	-23	-30	15	181	230
BHT	-10	-23	17	110	177
NNP	-7	-27	13	173	226

Table 3 - Cure Performance of Benzene Reducing Additives in Resin Anchor System

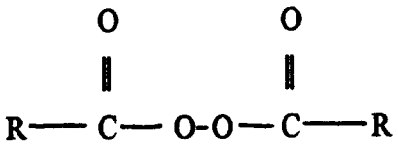
Additive	Time to maximum torque, sec	Maximum torque, m-g
None	48	3325
BHT	42	3625
NNP	42	664

The data in Table 2 clearly indicate a reduction of benzene formation and an improvement in stability of the BPO formulation, without any appreciable loss in performance. The system in Table 3 comprising BHT was similar in cure response to the control hardener which contained no additive. NNP did, however, adversely effect cure response, although benzene reduction was favorable. Thus, it is clear that end use applications are an important consideration in determining the type and amount of additive to be employed.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A method for reducing the rate and amount of hazardous by-product formation in diacyl peroxide formulations which generate hazardous by-products upon decomposition which comprises adding to said formulations at least one free-radical scavenger in an amount effective to reduce the rate of diacyl peroxide decomposition in said formulation.

2. The method of claim 1 wherein said diacyl peroxide is of the general formula:



wherein each R group may be the same or different and is selected from a substituted or unsubstituted aryl and aralkyl, alkyl or alkaryl group which generates hazardous by-products upon decomposition.

3. The method of claim 1 wherein said diacyl peroxide is dibenzoyl peroxide, or an ortho-, para-methyl or 2,4-dichloro derivative of dibenzoyl peroxide.

4. The method of claim 1 wherein said diacyl peroxide is dibenzoyl peroxide.

5. The method of claim 1 wherein said free-radical scavenger is selected from the group consisting of cinnamate esters, maleate esters, phenolic derivatives, triazinetrone derivatives, propionic esters, fumerate esters, oligomeric phosphonates, thiobisphenolics, phosphites, polythiodipropionates, thioesters, natural fatty acids, quinones, vitamin compounds and mixtures thereof.

6. The method of claim 5 wherein said free-radical scavenger is selected from the group consisting of 1,2-bis(3,5-di-t-butyl-4-hydroxyhydrocinnamoyl)hydrazine, octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate, tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane, dibutyl fumerate, dioctyl fumarate, dibutyl maleate, dioctyl maleate, linoleic acid, oleic acid, styrene phosphonis acid, calcium bis[monoethyl(3,5-di-t-butyl-4-hydroxybenzyl) phosphonate], benzoic acid, n-nonyl phenol, 2,6-di-t-butyl-4-methylphenol, triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-ethylphenyl)propionate], trisnonylphenylphosphite, t-butyl catechol, pyrrolidones, hydroquinone, toluhydroquinone, p-benzoquinone, mono-t-butylhydroquinone, 2,5-di-t-butylhydroquinone, hydroquinone monomethyl ether, Vitamin A, Vitamin C, Vitamin E, 1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, and mixtures thereof.

7. The method of claim 1 wherein said effective amount of free-radical scavengers is in the range of from about 0.001% - about 10% by weight based on the total weight of the diacyl peroxide formulation.

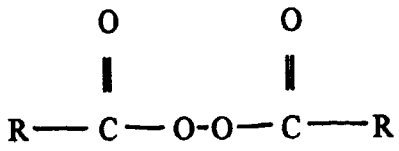
8. The method of claim 7 wherein said effective amount of free-radical scavenger is in the range of from about 0.01 -5% by weight based on the total weight of the diacyl peroxide formulation.

9. The method of claim 8 wherein said effective amount of free-radical scavenger is in the range of from about 0.1 -3% by weight based on the total weight of the diacyl peroxide formulation

10. The method of claim 1 wherein said diacyl peroxide formulation is a paste, emulsion, suspension or gel.

11. A diacyl peroxide formulation with improved stability and reduced hazardous by-product formation which comprises at least one diacyl peroxide which generates hazardous by-products upon decomposition, and at least one free-radical scavenger in an amount effective to reduce the rate of diacyl peroxide decomposition in said formulation.

12. The formulation of Claim 11 wherein said diacyl peroxide is of the general formula:



wherein each R group may be the same or different and is selected from a substituted or unsubstituted aryl and aralkyl, alkyl or alkaryl group which generates free benzene upon decomposition.

13. The formulation of claim 12 wherein said diacyl peroxide is dibenzoyl peroxide or an ortho-, para-methyl or 2,4-dichloro derivative of dibenzoyl peroxide.

14. The formulation of claim 13 wherein said diacyl peroxide is dibenzoyl peroxide.

15. The diacyl peroxide formulation of claim 11 wherein said formulation is a paste, emulsion, suspension or gel.

16. The formulation of claim 11 which additionally comprises water and plasticizer.

17. The formulation of claim 16 which additionally comprises an emulsifier, rheological additive and optionally, pigment.

18. The formulation of claim 11 wherein said free-radical scavenger is selected from the group consisting of cinnamate esters, maleate esters, phenolic derivatives, triazinetrone derivatives, propionic esters, fumerate esters, thiobisphenolics, phosphites, polythiodipropionates, thioesters, oligomeric phosphonates, natural fatty acids, quinones, Vitamin compounds and mixtures thereof.

19. The formulation of claim 18 wherein said free-radical scavenger is selected from the group consisting of 1,2-bis(3,5-di-t-butyl-4-hydroxyhydrocinnamoyl)hydrazine, octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate, tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane, dibutyl fumerate, dioctyl fumarate, dibutyl maleate, dioctyl maleate, linoleic acid, oleic acid, styrene phosphonis acid, calcium bis[monoethyl(3,5-di-t-butyl-4-hydroxybenzyl) phosphonate], benzoic acid, n-nonyl phenol, 2,6-di-t-butyl-4-methylphenol, triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-ethylphenyl)propionate], trisnonylphenylphosphite, t-butyl catechol, pyrrolidones, hydroquinone, toluhydroquinone, p-benzoquinone, mono-t-butylhydroquinone, 2,5-di-t-butylhydroquinone, hydroquinone monomethyl ether, Vitamin A, Vitamin C, Vitamin E, 1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, and mixtures thereof.

20. The formulation of claim 11 wherein an effective amount of free-radical scavenger is in the range of from about 0.001% - about 10% by weight based on the total weight of the diacyl peroxide formulation.

21. The formulation of claim 20 wherein said effective amount of free-radical scavenger is in the range of from about 0.01 - 5% by weight based on the total weight of the benzoyl peroxide formulation.

22. The formulation of claim 20 wherein said effective amount of free-radical scavenger is in the range of from about 0.1 - 3% by weight based on the total weight of the benzoyl peroxide formulation

23. A dibenzoyl peroxide formulation having reduced free benzene formation which comprises benzoyl peroxide and at least one free-radical scavenger in an amount to reduce the rate of benzoyl peroxide decomposition.

24. The formulation of Claim 23 which comprises 3-60 wt% of dibenzoyl peroxide and 0.001 to 10 wt% free radical scavenger.

25. The formulation of Claim 23 wherein said free-radical scavenger is selected from the group consisting of BHT, Irganox®1010, Irganox®1425, Vitamin E, NNP and mixtures thereof.

26. The formulation of Claim 23 which comprises 25 - 55% dibenzoyl peroxide and 0.1 - 3% by weight of a free-radical scavenger selected from the group consisting of BHT, Irganox®1010, Irganox®1425, Vitamin E, NNP and mixtures thereof.